

The University of Chicago

I. THE PEROXIDE EFFECT
IN THE ADDITION OF HYDROGEN
BROMIDE TO METHYL-
ACETYLENE

II. EXCHANGE REACTIONS OF
DEUTERIUM

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1936

By
JOHN GEORGE McNAB

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ACKNOWLEDGMENT

The author wishes to take this opportunity to acknowledge a great indebtedness to Professor M. S. Kharasch under whose careful supervision this research was conducted, and to Professor W. G. Brown for many valuable suggestions during the course of the second part of the work.

PART I

THE PEROXIDE EFFECT IN THE ADDITION OF HYDROGEN BROMIDE TO METHYLACETYLENE

Introduction

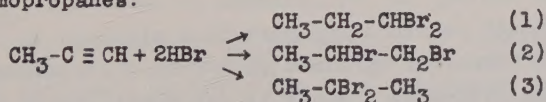
In previous communications from this laboratory Kharasch and his collaborators¹ have demonstrated the importance of peroxides in directing the addition of hydrogen bromide to olefinic hydrocarbons, in which the double bond is at the end of the chain. It seemed desirable to extend the investigation to the acetylene series, and so the addition of hydrogen bromide to methylacetylene was studied in some detail.

The experiments of Réboul² have previously shown that hydrogen bromide in aqueous solution adds to methylacetylene to yield 2,2-dibromopropane.

Addition of hydrogen bromide to methylacetylene.--It was found expedient, after a few preliminary experiments, to limit the investigation to a study of the final product formed by the addition of two moles of hydrogen bromide to methylacetylene. These experiments were carried out in the presence of peroxides and also in vacuo under peroxide-free conditions.

The structure of the molecule first formed, under peroxide-free conditions, by the addition of one mole of hydrogen bromide to methylacetylene, can be inferred readily from a consideration of the products isolated in this investigation, together with the work on the addition of hydrogen bromide to various bromopropylenes under way in this laboratory.

From structural considerations, it is obvious that methylacetylene can add two moles of hydrogen bromide to yield three dibromopropanes.



¹M. S. Kharasch and co-workers, *J. Am. Chem. Soc.*, **55**, 2468, 2521, 2531 (1933); **56**, 1642 (1934).

²M. Réboul, *Ann. chim.* (5), **14**, 365 (1878).

TABLE 1
ADDITION OF HYDROGEN BROMIDE TO METHYLACETYLENE*

Conditions	B. p., °C.	n_D^{20}	%1,2-dibromopropane	%2,2-dibromopropane
No agent added. Vacuum technique.....	112-115	1.4977	0	100
0.4 g. diphenylamine added to the methylacetylene. Vacuum technique.....	112-115	1.4977	0	100
0.2 g. thiocresol added to methylacetylene. Vacuum technique.....	112-115	1.4977	0	100
0.8 g. ascaridole added to methylacetylene, HBr passed in at -33°.....	139-142	1.5192	100	0
Same as above except vacuum technique used...	139-142	1.5193	100	0

*In all experiments 15 g. of methylacetylene and 91 g. of hydrogen bromide were used. The reaction mixture was allowed to stand for four days. The experiments recorded were checked many times. The yields were quantitative (95-100%).

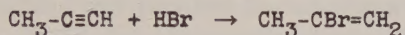
In all of the experiments, however, the reaction product proved to be the 2,2-dibromopropane, the 1,2-dibromopropane, or a mixture of these two compounds. The possibility of obtaining the 1,1-dibromopropane was not disregarded, but careful analysis of the reaction products (experimental part) revealed none of this compound.

Some of the experimental results are given in Table 1. A consideration of these data leaves little doubt regarding the striking effect peroxides exert in governing the direction of the addition. The 2,2-dibromopropane is formed when the reaction is allowed to take place in vacuo, and in the absence of any appreciable amounts of peroxides; on the other hand, 1,2-dibromopropane is formed exclusively in the presence of peroxides.

It should be mentioned here that although it is possible to obtain the "abnormal" product (1,2-) in the presence of added peroxides, the system as a whole is not particularly sensitive to traces of peroxides. This of course readily can be predicted from the fact that freshly prepared methylacetylene, or even material three to four days old, does not give a peroxide test,

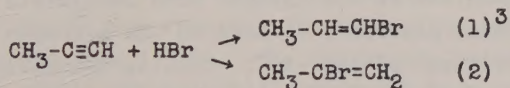
even though no precautions are used to exclude oxygen. Further corroboration of the low susceptibility of the system to the "peroxide effect" is found in the fact that the same product (2,2-dibromopropane) was formed whether the reaction was carried out in air, or in vacuo, or with antioxidants in vacuo. In this respect methylacetylene is similar to propylene,¹ and markedly different from halogen ethylenes, which are extremely sensitive even to traces of oxygen and (or) peroxides.

A critical consideration of this addition, in the light of our knowledge of the effect of peroxides on the direction of addition, points to the conclusion that the product of the non-catalyzed first addition of hydrogen bromide to methylacetylene should be 2-bromopropylene.



If the probability of a rearrangement is ignored (and there is not the slightest reason to assume it) then only 2-bromopropylene can yield the 2,2-dibromopropane under peroxide-free conditions. It is to be noted that from the standpoint of the theory developed in earlier papers,² the methyl group and the bromine atom in 2-bromopropylene reinforce each other in their directive effect, an interpretation in strict agreement with the exclusive formation of 2,2-dibromopropane under peroxide-free conditions.

The structure of the bromopropylene formed in the addition of hydrogen bromide to methylacetylene under peroxide conditions, is not deducible from a consideration of the present data.



In the light of the experience of Kharasch and his collaborators, the 1,2-dibromopropane should be the product formed

¹M. S. Kharasch and co-workers, loc. cit.

²Ibid.

³In this discussion the probability of formation of the cis-trans isomers of 1-bromopropylene, and the possibility of formation of different products due to a difference in the addition to the two stereoisomers has purposely been omitted. The justification for this omission rests upon the demonstration of the identity of the products formed in the addition of hydrogen bromide to many cis-trans isomers (M. C. McNab, Doctorate Dissertation, The University of Chicago, 1935).

by addition of hydrogen bromide to either (1) or (2) in the presence of peroxides. To check this prediction, the addition of hydrogen bromide to the isomeric bromopropylenes is now under way in this laboratory. However, it is clear that the information thus obtained may not give an unequivocal answer regarding the nature of the product when methylacetylene reacts with one mole of hydrogen bromide under peroxide conditions.

An experimental solution of the problem, namely, the actual isolation of the bromopropylene formed under peroxide-catalyzed conditions, is not very easy, because of the number of possible isomers, and particularly because of the greater sensitivity of the bromopropylenes to peroxides, which leads to the formation of large amounts of the 1,2-dibromopropane. A few preliminary experiments have convinced the author that both the theoretical and experimental objections to this approach are well justified.

Typical examples of experimental runs are recorded in Table 1. It was necessary to depart slightly from the standard Kharasch-Mayo technique in order to effect complete reversal of hydrogen bromide addition through the agency of peroxides. As a rule a tube containing the unsaturated compound was immersed in a bath of carbon dioxide and acetone, ascaridole added and hydrogen bromide bubbled into the mixture. When the required amount of hydrogen bromide had been introduced, the tube was sealed and allowed to stand at room temperature until the addition was complete. However, in the case of methylacetylene, in order to reverse the addition of the halogen acid completely by peroxides, it has been found necessary to pass in the hydrogen bromide at a temperature between -33 and -40° . This is undoubtedly due to the fact that ascaridole is but very slightly soluble in methylacetylene at the temperature of the carbon dioxide-acetone mixture.

Experimental Work

I. Technique of addition.--The usual Kharasch-Mayo¹ vacuum technique was employed in experiments involving the addition of hydrogen bromide under peroxide-free conditions. Quantitative yields of 2,2-dibromopropane were obtained in each case. In a few experiments using peroxides (ascaridole), the hydrogen bromide was bubbled into the mixture at -78° C. Only a partial

¹M. S. Kharasch and co-workers, loc. cit.

reversal in the addition was produced. However, it was observed that the ascaridole dissolved but slightly in the unsaturated hydrocarbon at the low temperature. In other experiments the ascaridole-methylacetylene mixture was allowed to stand for one hour in a bath of liquid ammonia (at which temperature the peroxide is appreciably dissolved) and hydrogen bromide introduced at a slow rate. In this case complete reversal was effected, the addition product being exclusively 1,2-dibromopropane.

II. Preparation of methylacetylene.--Methylacetylene was prepared in 200 g. lots by the action of dimethyl sulfate on a solution of sodium acetylide in liquid ammonia according to the method of Meinert and Hurd.¹ For the present investigation this was the best method, since the only impurity, acetylene, is readily removed by careful fractionation in a Davis column. Working with such relatively large quantities of materials, the experimental difficulties in this preparation (which is hard to carry out even on a small scale) were numerous. After some practice, however, pure methylacetylene was obtained in yields of 70-80 per cent. A sample of the product gave no test for peroxides.

III. Analysis and identification of products.--The reaction tubes were opened, allowed to stand for one hour to remove excess hydrogen bromide, the product weighed for yield and fractionally distilled three times in vacuo. This treatment was followed by washing with sodium bicarbonate solution and water, drying over calcium chloride and careful fractionation. The 1,2- and 2,2-dibromopropanes are distinguishable by their boiling points and can be separated to a large extent by repeated fractionations. Kharasch and Mayo² have reported the refractive index, n_D^{20} of 1,2-dibromopropane as 1.5194. The refractive index of 2,2-dibromopropane (not previously reported) was found to be 1.4977.³ Under peroxide-free conditions, a yield of 75 g. of product (100 per cent yield) was obtained, all of which boiled in a range of 3° (112-115°). This product is the 2,2-dibromopropane. In the presence of peroxides 75 g. of product was obtained all of which

¹R. N. Meinert and C. D. Hurd, J. Am. Chem. Soc., **52**, 4544 (1930).

²M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc., **55**, 2468 (1933).

³This substance was also prepared by direct bromination of isopropyl bromide. There was a perfect agreement of physical constants in the products obtained by the two methods.

distilled within the range 139-142° (1,2-dibromopropane). The 2,2-dibromopropane was further identified by conversion to acetone. Ten grams of the dibromide and 100 g. of water were heated at 160° for sixteen hours in a sealed tube. The acetone was distilled from the water solution and treated with 2,4-dinitrophenylhydrazine. The melting point of the product thus obtained was that given for the 2,4-dinitrophenylhydrazone of acetone (m. p. 128°). The melting point of a sample was not depressed when mixed with a known synthetic sample.

Summary

1. It has been shown that the "normal" addition of hydrogen bromide to methylacetylene produces exclusively 2,2-dibromopropane.
2. Under the influence of added peroxides, hydrogen bromide adds to methylacetylene to give 1,2-dibromopropane.
3. It has been found that the hydrogen bromide must be passed into the methylacetylene, containing the added peroxide, at a temperature of -33 to -40° in order to effect a complete reversal of the "normal" addition.

PART II

EXCHANGE REACTIONS OF DEUTERIUM

Introduction

During the past few years the increasing availability of water containing the hydrogen isotope of atomic weight two has made possible an extensive investigation of deuterium compounds. Through the medium of exchange reactions research workers in this field have been afforded a means of confirming many classical theories relevant to the nature of the hydrogen-to-oxygen, the hydrogen-to-nitrogen, and the hydrogen-to-carbon linkages. In all cases the observations have supported the convictions of both the organic and the inorganic chemists. In addition the velocity data derived from these investigations have been interesting in no small measure.

In 1933 Bonhoeffer and Brown¹ observed that the hydroxyl group hydrogens of sucrose exchanged immediately with deuterium of water-d₂ while the hydrogen atoms attached directly to carbon did not exchange. A similar result was obtained by Bonhoeffer and Rummel² in the case of cellulose. Exchange with water of only the alcoholic hydrogen atoms in ethylene glycol was reported by Hall³ and his collaborators. The exchange of hydroxyl group hydrogen atoms in the compounds mentioned above is probably the result of weak ionization. The reaction of amines with water-d₂ was studied by Goldfinger and Lasareff.⁴ In methylamine hydrochloride two hydrogen atoms (exclusive of the hydrogen of the acid) were found to undergo immediate exchange with deuterium, in dimethylamine hydrochloride only one. These observations confirm

¹K. F. Bonhoeffer and W. G. Brown, Zeits. f. physik. Chemie, **B23**, 171 (1933).

²K. F. Bonhoeffer and K. W. Rummel, Naturwiss., **22**, 45 (1934); Zeits. f. Elektrochem., **40**, 469 (1934).

³N. F. Hall, E. Bowden, and T. O. Jones, J. Am. Chem. Soc., **56**, 750 (1934).

⁴P. Goldfinger and W. Lasareff, Compt. rend., **200**, 1671 (1935).

the generally accepted structural formulas of these amino compounds but are at variance with that proposed by Thomsen,¹ namely $\text{CH}_2 = \text{NH}_3$, for which support had previously been evidenced in the spectroscopic data of Henri and Lasareff.² Reversible formation of $-\text{NH}_3^+$ is undoubtedly involved in the exchange of amino hydrogen atoms with water.

Hydrogen atoms attached to carbon were found to exchange slowly in the case of the aldehyde group,³ $-\text{CHO}$, for example, in acetaldehyde (one hydrogen atom exchanged) and formaldehyde (both hydrogen atoms exchanged), and in alkyl (methyl or methylene) radicals adjacent to a ketonic group, as in acetone and acetylacetone.⁴ The mechanism involved in the exchange in the aldehyde group is somewhat obscure but in the case of ketonic compounds mobility of the hydrogen atoms is undoubtedly the result of keto-enol tautomerism. It is interesting to note that in the ketones the rate of the isotopic exchange is markedly enhanced by the addition of small amounts of alkali and to a less extent by the presence of traces of acid.

Very limited success has been encountered in the study of the exchange reaction between heavy water and the hydrogen atoms of hydrocarbons in either the aliphatic or aromatic series. In saturated hydrocarbons no case of exchange has yet been reported. Attempts by Klar⁵ to effect an exchange between the hydrogen atoms of benzene and water containing deuterium were unavailing although Taylor⁶ and his associates recently obtained $\text{C}_6\text{H}_6\text{-d}_6$ by the reaction between water- d_2 and benzene at 200° over a nickel catalyst on kieselguhr. However, exchanges induced in this manner are of greater interest to investigators in the field of catalysis than to those concerned with a study of the nature of the general exchange reaction. In 1934 Reyerson and Yuster⁷ reported an isotopic exchange between acetylene and

¹Julius Thomsen, "Thermochemistry," 1908, p. 428.

²V. Henri and W. Lasareff, Compt. rend., **200**, 829 (1935).

³R. Klar, Zeits. f. physik. Chemie., **B26**, 335 (1934); K. F. Bonhoeffer and R. Klar, Naturwiss. **22**, 45 (1934).

⁴L. C. Anderson, J. O. Halford, and J. R. Bates, J. Am. Chem. Soc., **56**, 491 (1934); K. Schwartz and H. Steiner, Zeits. f. physik. Chemie., **B25**, 153 (1934).

⁵R. Klar, Zeits. f. physik. Chemie., **B26**, 335 (1934).

⁶P. I. Bowman, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., **57**, 960 (1935).

⁷L. H. Reyerson and S. Yuster, J. Am. Chem. Soc., **56**, 1426 (1934).

solutions of alkali in water-d₂. Experiments conducted in neutral and acid solution yielded negative results indicating that if exchange occurs in these cases it must take place with extreme slowness. The work of Reyerson and Yuster cannot, however, be accepted without some measure of doubt as subsequent investigation of the same reaction by Bell¹ did not confirm their results. If exchange does take place with acetylene, confirmatory evidence of the acidic nature of this compound is afforded.

From the viewpoint of the isotopic exchange reaction hydrogen atoms linked to carbon may be considered under two classes; in the first place, those whose exchange with deuterium involves the mechanism of keto-enol tautomerism and secondly, the non-enolizable type. It has already been observed that exchange of hydrogen atoms of the first class is catalyzed by both hydrogen and hydroxyl ions. Investigation of compounds containing hydrogen atoms of the second class has been, as yet, quite limited. Under the non-enolizable type of hydrogen atoms linked to carbon two divisions should be made. First, hydrogen atoms which have given evidence of possessing activity, for example, the hydrogen atoms involved in the formation of salts by many hydrocarbons, and secondly, atoms which appear extremely inactive, of which category the hydrogen atoms of normal saturated aliphatic hydrocarbons may be considered exemplary. Isotopic exchange of hydrogen atoms of the first division, if such an exchange should be observed, would be expected to proceed through a weak ionization.² Also, one would expect exchange in such cases to be subject to catalysis by hydroxyl ion. Only in the rather doubtful case of acetylene has such an isotopic exchange been observed. The exchange of hydrogen atoms of the second division, that is, inactive hydrogen atoms, could probably only be effected by catalysts other than acids or alkalies.

¹R. P. Bell, *J. Am. Chem. Soc.*, **57**, 778 (1935).

²It should be mentioned here that J. B. Conant and G. W. Wheland (*J. Am. Chem. Soc.*, **54**, 1212 [1932]) have outlined a classification of hydrocarbons and certain related compounds as extremely weak acids. Their work has recently been extended by W. K. McEwen (*ibid.*, **58**, 1124 [1936]). On the basis of the reaction:



the relative strength of many derivatives of water, ammonia, and methane as acids has been determined.

The possibility of distinguishing between hydrogen atoms of certain hydrocarbons and related compounds as active or inactive, through the medium of the isotopic exchange reaction, is apparent and to this end the present work was instituted. Since the limited solubility of the compounds under investigation in water-d₂ made use of this medium rather impractical, the exchange reaction was carried out using absolute ethyl alcohol containing deuterium in the hydroxyl group. The procedure adopted involved solution of the compound in the deuterio-alcohol, subsequent separation of the alcohol by distillation in vacuo, and determination of the decrease, if any, in the deuterium content of the alcohol. Analysis of the alcohol-d₁ was accomplished by combustion to water, and determination of the isotopic composition of the water thus obtained, by means of the float method adapted for use on relatively small samples.

EXPERIMENTAL PART

In all experiments a carefully dried and weighed sample of the compound to be investigated was introduced along with a measured quantity of alcohol- d_1 into a reaction tube fitted with a specially designed valve, capable of holding a vacuum. The tube was cooled in a carbon dioxide-acetone bath, evacuated thoroughly, and sealed off. The reaction mixture was then allowed to stand for the length of time desired, in some cases at room temperature but usually at an elevated temperature, maintained by immersion of the tube in an electrically heated oil bath. After standing for the requisite period in the oil bath the reaction vessel was removed, a receiver attached by means of a ground glass joint and, after sealing the tube to the vacuum line the system above the valve was thoroughly evacuated. The tube was then opened by breaking the valve by means of a magnetic hammer and the alcohol distilled into the receiver. The receiving vessel was cooled to -78°C . in a carbon dioxide-acetone bath. The deuterium content of the alcohol thus recovered was determined by the method outlined above and described in detail in following paragraphs. Special mention should be made at this point of the caution exercised in no small measure throughout this work to use reaction tubes carefully cleaned to remove contaminations of foreign materials. Conflicting observations recorded in the literature on the isotopic exchange reaction have undoubtedly arisen from the unfortuitous and unsuspected presence of catalytic substances in certain cases. For this reason, all reaction tubes, preliminary to use in our experiments, were washed successively with alcohol, sulphuric acid-dichromate solution, and then a dozen times with distilled water with subsequent drying in vacuo.

Combustion of alcohol.--In order to adapt the procedure outlined above for the study of the isotopic exchange reaction (viz., the use of deuterio-alcohol instead of water- d_2) to investigation on an extensive scale it was obviously necessary to devise a method for burning alcohol samples to water in a manner economical from the standpoint of time consumption. To this end

the following process was adopted. The alcohol sample (about 1 c. c.) was first burned in a specially designed pyrex glass lamp with an asbestos wick fitted into a 200 c.c. bulb by means of a stopper provided with an inlet for the introduction of dry air. A short length of 10 mm. glass tubing sealed to the top of the bulb and bent at right angles to it was sealed to a short glass cap which fitted over the end of a quartz tube of 1 inch bore and 30 inches in length. The other end of the quartz tube was fitted with a similar glass cap sealed to a 10 mm. tube leading to receivers in the form of traps. The glass caps were cemented tightly to the quartz tube by means of a heat-resisting alundum-sodium silicate mixture. The quartz tube contained a 12 inch bed of copper oxide and was heated electrically to a temperature of 750°C. Vapors from the flame of the alcohol lamp were drawn by slight suction through the hot copper oxide bed of the quartz tube and were condensed in two traps placed in series and surrounded by carbon dioxide-acetone baths. The air stream drawn through the apparatus was carefully dried by passage through calcium chloride towers 10 feet in total length before it entered the bulb containing the lamp. Through this combination of the lamp with the copper oxide treatment complete combustion of alcohol was readily and efficiently effected, the time required for a 1 c.c. sample of alcohol being about 10 minutes. Preliminary experiments conducted to test the possibility of using the lamp alone to burn alcohol to water showed that products of intermediate oxidation contaminated the water samples obtained in amounts of such magnitude as to prohibit the application of this method if accurate and consistent results were to be achieved.

Analysis of water samples: An adaptation of the float method for determining the isotopic composition of small quantities of water.--One of the most widely used methods for the determination of the isotopic composition of water samples has been that based on density measurements. In this work the pycnometer has served with advantage to produce highly accurate results. However, despite the great precision of which this apparatus is capable, its use has been restricted because of the time required to make determinations.

Dufour¹ first recognized the possibility of determining slight differences in the densities of two samples of water by

¹H. Dufour, Compt. rend. 24, 1080 (1862).

means of the buoyancy balance. The apparatus devised by this investigator was later improved by Richards¹ and his associates. In 1933 Lewis and Macdonald² introduced the principle for the determination of deuterium in water. The method involves the use of a glass float, so constructed as to remain just suspended in the reference sample at a convenient temperature. In the unknown sample the float will remain suspended at a different temperature. The difference in the temperatures at which the float remains static in the two samples of water serves to determine the density of the unknown and subsequently its deuterium concentration. The advantage of the method is greatest where the analysis of water only slightly greater in deuterium content than natural water is concerned.

Since the water samples in our work were obtained from the combustion of alcohol it was obviously important to employ a method of analysis which would permit the use of a relatively small quantity of water. To the attainment of this end a procedure involving a float much smaller than any previously employed in the field of relative density determinations was developed. In preliminary experiments floats of pyrex glass were constructed but in later work a float of clear quartz was used.³ This float was constructed in the form of a small bulb about 6 mm. in diameter with a short tail attached. The temperature at which it just remained suspended in natural water, or, what we have chosen to call the "floating" temperature, was about 22°C. With this piece of apparatus it was possible to determine the isotopic composition of water samples of 1/2 c.c. magnitude.

In the determination of the "floating" temperature the float was placed in a tube containing the water. The tube was of 10 mm. bore, about 6 inches in length, and a ground glass joint formed the open end. The float was kept immersed in the water at all times by means of a glass rod attached to the other member of the ground joint and dipping just below the surface of the water. The tube was placed in a thermostat, constructed to permit, on the one hand, a rather rapid changing in temperature over the short

¹T. W. Richards and G. W. Harris, J. Am. Chem. Soc., **38**, 1000 (1916).

²G. N. Lewis and R. T. Macdonald, J. Chem. Phys., **1**, 341 (1933).

³The author wishes to express his gratitude to Professor W. G. Brown who devoted many hours of skillful and painstaking work to the construction of the floats used in this research.

range necessitated, and, on the other hand, a control of the temperature to within a few one-thousandths of a degree at any point within the range. The movement of the float in the water was observed through a microscope affording 10-fold magnification and the temperature was adjusted to the point where the float just remained suspended in the body of the water. In general, a period of five minutes was sufficient for a determination of the "floating" temperature.

The float was calibrated by observing the temperature at which it just remained suspended in a sample of very pure natural water and in a reference sample of known density (determined pycnometrically) containing deuterium. As the water samples under investigation in our work were obtained from the combustion of alcohol it was necessary to check the isotopic composition of water obtained from the combustion of pure light alcohol with that of natural water. Several determinations showed the densities of water samples from the two sources to differ only by a few parts per million, a figure within the range of experimental error.

Calibration of the float.--The reference water used in the float calibration was obtained by dilution of a small quantity of water containing approximately 12 per cent deuterium oxide to a concentration of about .5 per cent by adding carefully purified natural water. The exact composition of the 12 per cent (approximate) water was determined by pycnometrical measurement of the density and subsequent calculation of the deuterium content. For this water the density d_{25}^{25} , was found to be 1.01326. From Lewis and Luten's¹ equation:

$$d = 1.00000 + 0.1056N_2 - .0012N_1N_2$$

for the relationship between density and mol fraction in water containing deuterium, corrected to $d_{25}^{25} = 1.10740$ for 100 per cent water- d_2 ,² the concentration of the water was determined at 12.47 per cent deuterium oxide. To 4.1833 g. of this water was added 99.5169 g. of carefully purified natural water in the preparation of the reference sample. The consequent concentration of this reference sample was 0.503 per cent water- d_2 . In Table 1

¹G. N. Lewis and D. B. Luten, Jr., J. Am. Chem. Soc., **55**, 506 (1933).

²L. Tronstad, J. Nordbagen, and J. Brun, Nature, **136** (515) 1934. The value 1.1074 for $d_{25}^{25} = 1.1074$ for 100 per cent H_2O is the most recent for this quantity.

are recorded the "floating" temperature measurements involved in the calibration of the float. From the average value for the "floating" temperature of pure natural water, 1.625° , and that for the reference water (0.503 per cent H_2^{20}), 3.665° , the "floating" temperature coefficient of 0.0041° for a change in deuterium concentration of one part per hundred thousand is obtained. In the analysis of water of unknown deuterium content, realization of the sensitivity exhibited in the measurements of the "floating" temperature ($\pm 0.040^{\circ}$) of the water samples of Table 1 would reflect determination of deuterium content to within one part in ten thousand. To test the precision of the method further, water containing a concentration of deuterium unknown to the author was subjected to analysis. "Floating" temperature readings of 2.570° , 2.570° , and 2.565° were observed in successive determinations. The concentration of water- d_2 calculated from these measurements was 0.24 per cent, a value which was in good agreement with that (0.25 per cent) obtained by a different method of isotopic analysis by another investigator. The very close agreement of the "floating" temperature readings in this particular case was undoubtedly fortuitous but from all the determinations conducted the consistency obtainable proved to be within ± 0.1 per cent in deuterium concentration ($\pm 0.040^{\circ}$ in "floating" temperature readings). In the case of water samples containing deuterium resulting from combustion of deuterio-ethyl alcohol (data recorded later) such precision was not achieved. However, this was hardly to be expected in view of the fact that certain unavoidable manipulations of the absolute alcohol- d_1 are involved.

Purification of water samples.--The importance of the purity of the water and the cleanliness of the float and containing tube employed in the analysis for deuterium by the float method deserves special emphasis. Even minute contaminations militate against the attainment of reproducible results. In the present work the water obtained from the combustion of alcohol was distilled in vacuo from the traps into a receiver fitted by a ground joint to a manifold on the vacuum line. In this receiver the sample was treated with a trace of alkali and potassium permanganate at $60\text{--}70^{\circ}\text{C.}$ for half an hour. The water was then sublimed four times in vacuo. In the final sublimation the sample was trapped in the tube in which the subsequent float method analysis was carried out. The float itself was washed thoroughly

TABLE 1*

No.	Source of Water	"Floating" Temperature
1	Natural water	1.610
2	" "	1.625
3	" "	1.610
4	" "	1.650
5	Combustion of	1.605
6	absolute alcohol	1.625
7	" "	1.655
8	" "	1.610
9	" "	1.620
10	" "	1.645
11	Reference water	3.620
12	(0.503% D_2O)	3.695
13	" "	3.660
14	" "	3.675
15	" "	3.670

*The values for the "floating" temperature were obtained by the use of a differential Beckman thermometer.

at regular intervals with very dilute sulfuric acid-potassium dichromate solution and then several times with redistilled water. It was dried in a confined space at room temperature and atmospheric pressure as its sensitive nature did not permit the use of vacuum technique in this operation.

Preparation of alcohol- d_1 .--Ethyl alcohol with part of the hydroxyl group hydrogen replaced by deuterium was prepared by the action of 99.5 per cent water- d_2 on absolute alcohol. To insure the anhydrous character of the alcohol used in this work a quantity of absolute alcohol prepared by refluxing over calcium oxide was distilled through a fractionating column from 5 per cent of its weight of sodium. A fraction of constant boiling point (78.3°) was collected under anhydrous conditions. To 194 g. of this product about 4.2 g. of 99.5 per cent heavy water was added. Through a hydrogen-deuterium exchange alcohol containing about 10 mol per cent of deuterium should result.¹ The mixture was allowed to stand for a short time and then subjected to prolonged refluxing over freshly baked lime to remove the mixture of light and heavy water

¹A recent paper by W. J. C. Orr (Trans. Far. Soc., **32**, 1033 [1936]) has revealed the rather surprising fact that exchange between water- d_2 and ethyl alcohol requires a period of 18 hours at room temperature to reach completion.

present subsequent to the isotopic exchange. The alcohol containing deuterium was then distilled from the lime, collected under anhydrous conditions and stored in an hermetically sealed container.

Analysis of alcohol-d₁ for deuterium content.--The water samples obtained from combustion of several portions (about 1 c.c. each) of the deuterio-alcohol were subjected to analysis for isotopic composition by the float method. "Floating" temperature readings were 7.380°, 7.380°, 7.485°, 7.365°, 7.370°, 7.330°, 7.425°, 7.385°, and 7.335°, mean 7.385°. Assuming a linear relationship between "floating" temperature and deuterium concentration,¹ the latter can be calculated from the following equation:

$$X = \frac{X_2(T - T_1)}{(T_2 - T_1)}$$

where X represents the concentration of deuterium in water of unknown concentration, X₂ the concentration of deuterium in the known sample, and T, T₁, and T₂ respectively, the "floating" temperature readings of the unknown water, pure natural water, and the sample of known water. On this basis the isotopic composition of water resulting from combustion of the deuterio-alcohol was calculated to be 1.42 per cent deuterium oxide, from which the concentration of deuterium in the alcohol-d₁ is determined at 7.10 per cent.

It has been mentioned previously that, ordinarily, analyses of water containing deuterium could be duplicated to within ±.01 per cent in deuterium concentration. In the analyses of water samples derived from combustion of deuterio-alcohol recovered from exchange reaction experiments this sensitivity was not realized but the results in these cases were always consistent to within ±.02 per cent in deuterium ("floating" temperature measurements checking to within ±.080°). "Floating" temperature readings of water resulting from combustion of the alcohol-d₁ used in the experiments were not regarded as significant of exchange unless they were lower than 7.385° (the "floating" temperature of water from the stock alcohol-d₁) by more than 0.100°.

The decrease in the deuterium content of the alcohol-d₁ incurred through use in exchange reaction experiments can be

¹Such an assumption is not entirely justifiable in view of the fact that the expansion of water is not a linear function of the temperature but for our purposes the error involved was considered negligible.

calculated from the difference in the "floating" temperatures of the water resulting from combustion of the deuterio-alcohol before and after use in the experiments. This decrease is indicative of the extent to which isotopic exchange has taken place.

The decrease in deuterium content of the alcohol- d_1 to be expected through exchange with hydrogen atoms of the compound investigated can be predicted to some extent by calculations based on the assumption of a statistical distribution of deuterium atoms between the reaction components. Such calculations cannot, however, be accorded a great significance since the actual distribution of deuterium atoms between molecules is dependent on the equilibrium constant. Deviations from this circumstance are certainly to be expected in most cases of liquid phase reactions. For the calculation of the decrease in deuterium content of the alcohol- d_1 to be expected in any exchange reaction on the basis of a simple distribution of deuterium, the following formula has been developed:

$$X = \frac{m}{n} \left(\frac{A_1}{A_2} - 1 \right)$$

where X represents the number of replaceable hydrogen atoms in the compound, RH_x , of which n mols are dissolved in m mols of alcohol- d_1 of initial deuterium concentration, A_1 , and final concentration, A_2 .

Experimental Results

In general the reaction mixtures used consisted of a 5 g. portion of the compound under investigation and 5 c.c. of deuterio-alcohol. In the case of liquid substances 5 c.c. quantities were employed. In all experiments the reaction tubes were sealed in vacuo and recovery of the alcohol- d_1 after reaction was effected through use of vacuum technique in order to avoid, as far as possible, the error inherent in manipulations involving absolute alcohol. It is apparent that a relatively large amount of compound to that of alcohol- d_1 was employed in the exchange reaction experiments. This procedure was necessary as the molecular weights of many of the substances studied were quite large and in small amounts of these only very small fractions of a gram atomic weight of replaceable hydrogen would be present. In order to effect an appreciable decrease in the deuterium content of the alcohol by isotopic exchange, therefore, the relatively large amounts of the compounds were employed in the experiments. As

the reaction tubes in most cases were allowed to stand in an oil bath at an elevated temperature complete solution of the compounds in the alcohol-d₁ was effected. Under each experiment recorded below is to be found (a) the "floating" temperature of water obtained from combustion of the stock alcohol-d₁ and (b) the "floating" temperature readings of the water resulting from combustion of the alcohol-d₁ sample recovered after use in the exchange reaction experiment. The values given in (b) include the individual "floating" temperature readings observed and the mean. The value for (a) is repeated under each experiment to facilitate comparison with those of (b), the latter, of course, being specific for each experiment.

Triphenylmethane.--The triphenylmethane used in the present work was carefully purified by several crystallizations from alcohol. The compound was dried thoroughly in vacuo to remove any traces of water and solvent of crystallization: m. p. 92°.

Experiment 1.--A reaction tube containing 5 g. of triphenylmethane and 5 c.c. of deuterio-alcohol was allowed to stand at room temperature for 133 days. (a) 7.385°; (b) 7.285°, 7.260°, 7.460°; mean 7.335°

Experiment 2.--A reaction mixture identical with that of experiment 1 was maintained at a temperature of 100° for 150 days. (a) 7.385°; (b) 7.350°, 7.400°, 7.410°; mean 7.385°.

Experiment 3.--To a reaction mixture of 5 g. triphenylmethane and 5 c.c. alcohol-d₁ 0.002 g. NaOH was added. The reaction tube was immersed in an oil bath at 100° for 6 days. The error introduced by the presence of such a small quantity of alkali is of negligible magnitude. (a) 7.385°; (b) 7.470°, 7.400°; mean 7.435°.

Diphenylmethane.--This compound was purified prior to use by a series of vacuum distillations.

Experiment 4.--The exchange reaction solution of diphenylmethane and alcohol-d₁ was allowed to stand at room temperature for 147 days. (a) 7.385°; (b) 7.355°, 7.375°; mean 7.365°.

Fluorene.--A pure sample of this compound was obtained by several crystallizations from alcohol with subsequent drying in vacuo: m. p. 112-114°.

Experiment 5.--A reaction tube containing 5 g. fluorene and 5 c.c. deuterio-alcohol stood at room temperature for 138 days. (a) 7.385°; (b) 7.410°, 7.430°, 7.425°; mean 7.420°.

Experiment 6.--The reaction tube containing fluorene in solution in alcohol- d_1 at 110° was allowed to stand for 28 days. (a) 7.385° ; (b) 7.285° , 7.335° ; mean 7.310° .

Experiment 7.--A reaction mixture of 5 g. fluorene and 5 c.c. alcohol- d_1 containing .002 g. of NaOH was heated to 110° for 8 days. (a) 7.385° ; (b) 5.415° , 5.255° ; mean 5.340° .

Experiment 8.--A reaction mixture identical with that of experiment 7 was heated to a temperature of 110° for 2 days. (a) 7.285° ; (b) 5.510° , 5.375° ; mean 5.440° .

Experiment 9.--A reaction mixture of 5 g. fluorene and 5 c.c. deuterio-alcohol 0.01 molar in H_2SO_4 was maintained at a temperature of 110° for 2 days. (a) 7.385° ; (b) 7.395° , 7.465° ; mean 7.430° .

Acenaphthene.--A pure vacuum dried product was prepared for use in this work. M. p. $94-95^{\circ}$.

Experiment 10.--A 5 g. portion of acenaphthene was placed in a reaction tube with 5 c.c. alcohol- d_1 and the tube immersed in an oil bath at 110° for 36 hours. (a) 7.385° ; (b) 7.430° , 7.400° ; mean 7.415° .

Dianisylphenylmethane.--A quantity of this compound was purified by several crystallizations from a mixture of chloroform and methyl alcohol. Drying was effected in vacuo. M. p. $100-101^{\circ}$.

Experiment 11.--A reaction mixture of dianisylphenylmethane and deuterio-alcohol was maintained at a temperature of 110° for 36 hours. (a) 7.385° ; (b) 7.340° , 7.370° ; mean 7.355° .

Experiment 12.--A reaction mixture of dianisylphenylmethane and alcohol- d_1 .02 molar in NaOH was heated to a temperature of 110° for a period of 96 hours. (a) 7.385° ; (b) 7.060° .

Ethyl acetoacetate.--The product used in this work was purified by distillation in vacuo.

Experiment 13.--A reaction tube containing 5 c.c. ethyl acetoacetate and 5 c.c. alcohol- d_1 was allowed to stand at room temperature for 3 days. (a) 7.385° ; (b) 5.125° , 4.940° ; mean 5.030° .

Succinimide.--A pure sample of this compound was dried for several hours in an Abderhalden desiccator at 78° prior to use in the exchange experiments. M. p. 124° .

Experiment 14.--A reaction mixture of 5 g. succinimide and 5 c.c. deuterio-alcohol was maintained at a temperature of

110° for a period of 25 hours. (a) 7.385°; (b) 5.450°, 5.640°; mean 5.520°.

β-naphtholmethyl ether.--A carefully purified sample of this compound was thoroughly dried in vacuo for use in the present work. M. p. 70°.

Experiment 15.--A tube containing the *β*-naphtholmethyl ether and alcohol-d₁ was immersed in an oil bath at 110° for 22 hours. (a) 7.385°; (b) 7.435°, 7.395°; mean 7.420°.

Experiment 16.--A reaction mixture of *β*-naphtholmethyl ether and deuterio-alcohol containing .002 g. of NaOH was heated to a temperature of 110° for 22 hours. (a) 7.385°; (b) 7.425°, 7.365°; mean 7.395°.

o-Nitrotoluene.--The product used in the present work was purified by distillation in vacuo.

Experiment 17.--A solution of *o*-nitrotoluene in alcohol-d₁ was heated to a temperature of 110° for 34 hours. (a) 7.385°; (b) 6.400°, 6.470°; mean 6.435°.

Experiment 18.--A reaction mixture of *o*-nitrotoluene and alcohol-d₁ .02 molar in NaOH was maintained at a temperature of 110° for 34 hours. (a) 7.385°; (b) 5.565°, 5.615°; mean 5.590°.

p-Nitrotoluene.--A purified sample of this compound was dried thoroughly in vacuo prior to use in the exchange reaction experiments: m. p. 52°.

Experiment 19.--A reaction tube containing 5 g. *p*-nitrotoluene and 5 c.c. deuterio-alcohol was immersed in an oil bath at 110° for 48 hours. (a) 7.385°; (b) 7.290°, 7.260°; mean 7.275°.

Experiment 20.--A reaction mixture of *p*-nitrotoluene and alcohol-d₁ .02 molar in NaOH was heated to 110° for 48 hours. (a) 7.385°; (b) 6.250°, 6.210°; mean 6.230°.

Quinaldine.--A quantity of this compound was purified prior to use by distillation in vacuo.

Experiment 21.--A reaction tube containing 5 c.c. quinaldine in solution in 5 c.c. deuterio-alcohol was heated to a temperature of 110° for a period of 60 hours. (a) 7.385°; (b) 4.795°, 4.845°; mean 4.820°.

Trinitrobenzene (1,3,5-).--A pure sample of this compound was dried thoroughly in vacuo for use in the present investigation: m. p. 121-122°.

Experiment 22.--A reaction mixture of 5 g. 1,3,5-trinitrobenzene and 5 c.c. alcohol-d₁ was maintained at a temperature of

110° for 64 hours. (a) 7.385°; (b) 7.345°, 7.395°; mean 7.370°.

Experiment 23.--A reaction mixture of 1,3,5-trinitrobenzene and deuterio-alcohol .02 molar in NaOH was heated to a temperature of 110° for a period of 68 hours. (a) 7.385°; (b) 5.075°, 5.015°; mean 5.045°.

β -naphthoquinaldine.--This compound was purified by distillation under a very low pressure. M. p. 82°.

Experiment 24.--A reaction mixture of β -naphthoquinaldine and deuterio-alcohol was heated to a temperature of 110° for 104 hours. (a) 7.385°; (b) 6.150°, 6.090°; mean 6.120°.

Experiment 25.--A reaction mixture of β -naphthoquinaldine and alcohol-d₁, .02 molar in NaOH was maintained at 110° for 108 hours. (a) 7.385°; (b) 5.050°, 5.120°; mean 5.085°.

In Table 2 are recorded the experimental observations described above. Columns 3 and 4 of the table show a comparison between the decrease in the deuterium content of the alcohol-d₁ observed in the exchange experiments and the decrease predicted on the basis of a statistical distribution of the deuterium atoms between the reaction components.

TABLE 2

Compound	Conditions	Decrease in deuterium of alc. (observed)	Decrease in deuterium of alc. (calculated)
Triphenylmethane	Room temp. for 135 days	0	19% for exchange of one H atom
Triphenylmethane	100° for 150 days	0	"
Triphenylmethane	100° for 6 days. .02 M. in NaOH	0	"
Diphenylmethane	Room temp. for 147 days	0	41% for exchange of two H atoms
Fluorene	Room temp. for 138 days	0	41% for exchange of two H atoms
Fluorene	110° for 28 days	0	41% for exchange of two H atoms
Fluorene	110° for 8 days .02 M. in NaOH	35.5%	"
Fluorene	110° for 2 days .02 M. in NaOH	32.5%	"

TABLE 2 (Continued)

Compound	Conditions	Decrease in deuterium of alc. (observed)	Decrease in deuterium of alc. (calculated)
Fluorene	110° for 2 days .01 M. in H ₂ SO ₄	0	41% for exchange of two H atoms
Acenaphthene ...	110° for 36 hours	0	60% for exchange of four H atoms
Dianisylphenyl-methane	110° for 36 hours	0	15.5% for exchange of one H atom
Dianisylphenyl-methane	110° for 96 hours .02 M. in NaOH	5.5%	"
Ethyl acetoacetate	Room temp. for 3 days	41.0%	47.5% for exchange of two H atoms, 69.5% for five H atoms
Succinimide	110° for 25 hours	31.5%	36.5% for exchange of two H atoms
β -naphthol methyl ether ..	110° for 22 hours	0	26.5% for exchange of one H atom
β -naphthol-methyl ether ..	110° for 22 hours .02 M. in NaOH	0	"
o-Nitrotoluene .	110° for 34 hours	17.0%	33% for exchange of one H atom, 59.5% for three H atoms
o-Nitrotoluene .	110° for 34 hours .02 M. in NaOH	31.5%	"
p-Nitrotoluene .	110° for 48 hours	Very little, if any	"
p-Nitrotoluene .	110° for 48 hours .02 M. in NaOH	20.0%	"
Quinaldine	110° for 60 hours	45.0%	32% for exchange of one H atom, 58.5% for three H atoms
1,3,5-Trinitrobenzene	110° for 64 hours	0	44% for exchange of three H atoms
1,3,5-Trinitrobenzene	110° for 68 hours .02 M. in NaOH	40.0%	"

TABLE 2 (Concluded)

Compound	Conditions	Decrease in deuterium of alc. (observed)	Decrease in deuterium of alc. (calculated)
β -Naphtho-quinaldine	110° for 104 hours	21.5%	47% for exchange of three H atoms
β -Naphtho-quinaldine	110° for 108 hours .02 M. in NaOH	40.5%	"

Discussion

The foregoing experimental observations have shown that, of the hydrocarbons studied, namely, triphenylmethane, dianisylphenylmethane, diphenylmethane, acenaphthene, and fluorene, only in the cases of the last-mentioned and dianisylphenylmethane was a hydrogen-deuterium exchange effected. Furthermore, only under the catalytic influence of a trace of alkali was exchange accomplished in these cases. Catalysis by hydroxyl ion is readily explained in the light of its character as a proton acceptor. An attempt was made to effect exchange of the hydrogen atoms of fluorene through the agency of hydrogen ions by adding a trace of sulfuric acid to the fluorene-alcohol- d_1 reaction mixture, but no success was encountered. In experiment 7 a complete (equilibrium) exchange of the two methylene group hydrogen atoms of fluorene was observed in a period of 8 days. In the succeeding experiment a similar result was achieved in 48 hours. It was decided, however, to reserve further study of the very important problem of reaction velocity in this and in other cases for future investigation. The exchange reaction observations from the experiments with hydrocarbons are somewhat surprising in view of the fact that, like fluorene, triphenylmethane forms a stable sodium salt. If salt formation is regarded as a criterion of acidity one would expect to find an isotopic exchange taking place in triphenylmethane. This was not observed, however, and it appears that some factor other than acid ionization may be involved in the formation of salts by compounds such as triphenylmethane. At least it can be said that the lability of the methylene group hydrogen atoms of fluorene is greater than that of the aliphatic hydrogen atom of triphenylmethane. The possibility of illustrating relative degrees of lability of hydrogen atoms in certain

hydrocarbons and related compounds by a study of the isotopic exchange reaction, either from reaction velocity determinations or investigation of the amount of alkali required to effect exchange in a given period of time, is apparent from the present work.

In the study of the isotopic exchange reaction between ethyl acetoacetate and deuterio-alcohol a decrease of 41 per cent in the deuterium content of the alcohol- d_1 was observed after the reaction mixture had stood for 3 days at room temperature. The decrease predictable on the basis of a statistical distribution of deuterium between the components is, for exchange of two hydrogen atoms, 47 per cent; for five hydrogen atoms, 70 per cent. It would appear from these data that either complete (equilibrium) exchange of the two methylene group hydrogen atoms of the compound had taken place in the time allowed, or, less probably, that the five hydrogen atoms attached to the carbon atoms adjacent to the carbonyl group had undergone a partial exchange.

In the case of succinimide a decrease in the deuterium content of the alcohol- d_1 to the extent of 31.5 per cent was observed in the exchange reaction investigation. As a statistical distribution involving the exchange of one hydrogen atom would predict a loss of 33 per cent in the deuterium content of the alcohol, it is apparent that only the imino hydrogen atom in succinimide underwent exchange.

In the experiments on *β*-naphtholmethyl ether no hydrogen-deuterium exchange was found to take place even under the influence of a trace of alkali. The lability of hydrogen atoms in certain positions characteristic of many substituted naphthalenes was not illustrated in the present experiments.

There is considerable evidence for the existence of the nitronic acid tautomer of o-nitrotoluene. In the present investigation hydrogen-deuterium exchange to some extent was observed between o-nitrotoluene and deuterio-alcohol. The exchange was catalyzed by a trace of alkali. With p-nitrotoluene very slight, if any, exchange took place in neutral solution but partial exchange of the methyl group hydrogens was observed under the catalytic influence of hydroxyl ion. These experiments afford confirmatory evidence of the lability of the aliphatic hydrogen atoms of o-nitro and p-nitrotoluene.

Evidence for the activity of nuclear hydrogen atoms in

nitro substituted aromatic compounds has been established by the investigation of the isotopic exchange reaction between 1,3,5-trinitrobenzene and alcohol- d_1 . In neutral solution no exchange was evidenced, but recovery and analysis of the alcohol- d_1 from a reaction mixture .02 molar in sodium hydroxide revealed a decrease in deuterium content of the deuterio-alcohol of 40 per cent. The decrease expected for exchange of 3 hydrogen atoms in the light of a simple distribution of deuterium was 44 per cent.

A suspected lability of the hydrogen atoms in the methyl group of quinaldine was confirmed by experiments with this compound. In neutral solution a 46 per cent decrease in the deuterium content of the alcohol- d_1 , recovered after 60 hours contact with quinaldine at 110° , was observed. Statistical distribution figures predicted a decrease of 58 per cent for exchange of 3 hydrogen atoms. Similar results were obtained with β -naphthoquinaldine.

SUMMARY

1. The buoyancy balance method for relative density determinations has been adapted for the isotopic analysis of small samples (1/2 c.c.) of water containing low concentrations of deuterium. The use of a very small float constructed of clear quartz is involved.

2. A technique for the investigation of the hydrogen-deuterium exchange reaction in certain organic compounds, where the use of water- d_2 is impractical from solubility considerations, has been developed. In this work deuterio-ethyl alcohol was employed as solvent and source of deuterium for the study of the isotopic exchange reaction.

3. The exchange reaction was investigated in the cases of several hydrocarbons and simple derived compounds containing reputed labile or active hydrogen atoms. The compounds studied included triphenylmethane, dianisylphenylmethane, diphenylmethane, fluorene*, acenaphthene, acetoacetic ester*, succinimide*, β -naphtholmethyl ether, o-nitrotoluene*, p-nitrotoluene*, 1,3,5-trinitrobenzene*, quinaldine*, and β -naphthoquinaldine*. In the cases of the compounds marked with an asterisk isotopic exchange was observed.

